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(54) Abstract Title

Organic opto-electronic device

(57) An opto-electronic device comprising, a anode 10, a light transmissive cathode 11 and an opto-electronically active region 12 of organic material located between the electrodes; the light-transmissive cathode including an electrically conducting layer 11b and a spacing layer 11a comprising an electrically non-conducting material, the spacing layer located between the electrically conducting layer and the active layer and being sufficiently thin. The non-conducting material may be CsF, LiF, Li₂O or a mixture thereof and may additionally comprise a thin layer of Al, Ag or Au. Light 30 may be emitted from either/both face(s) of the device.

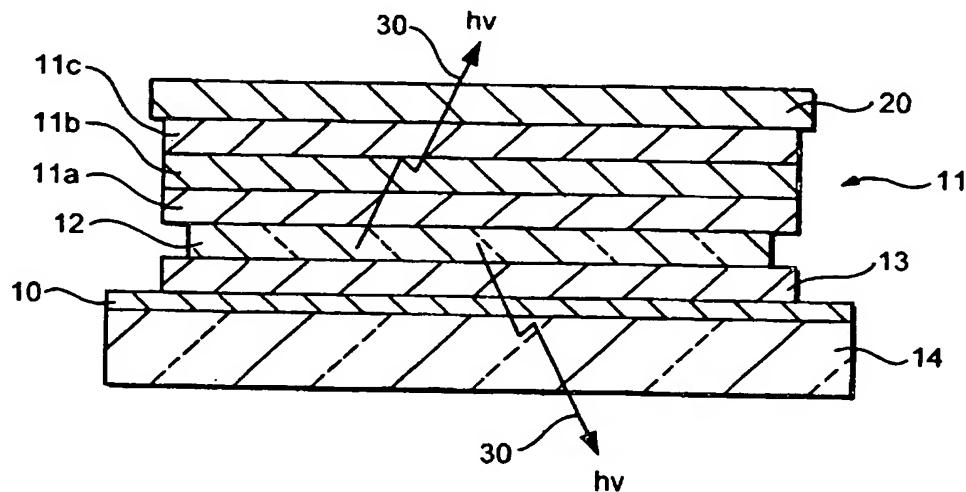


FIG. 2

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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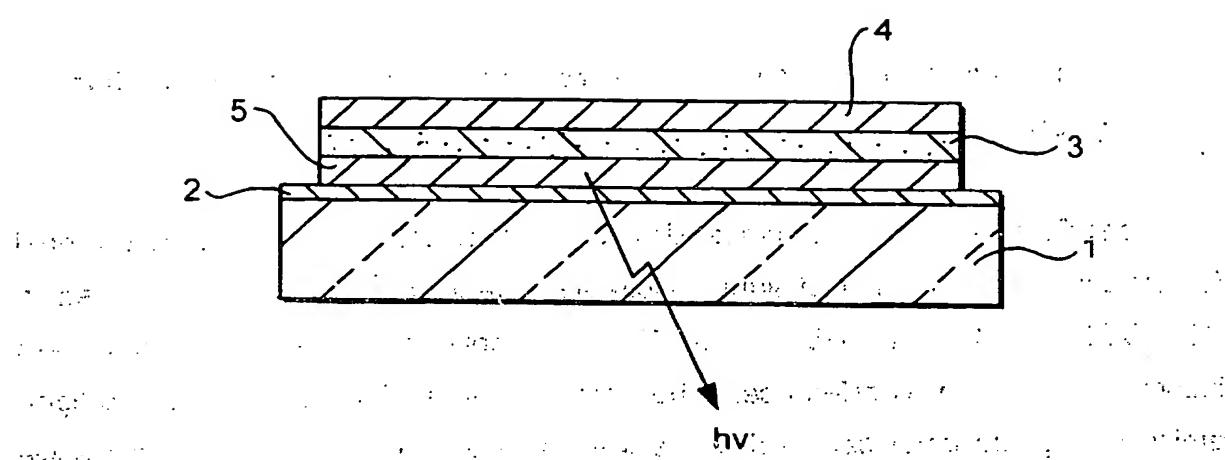


FIG. 1

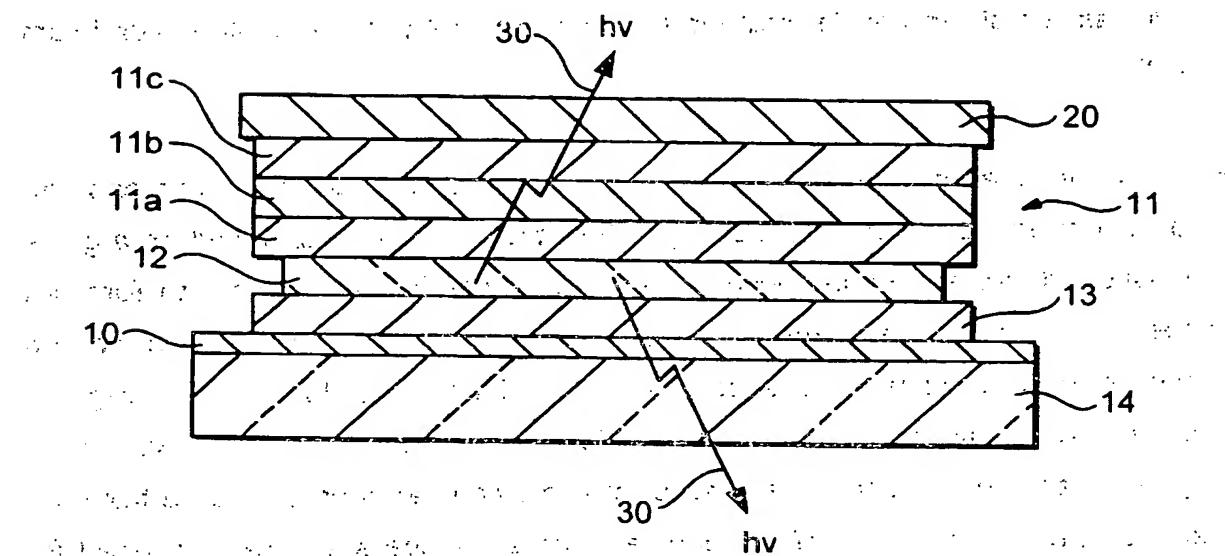


FIG. 2

OPTO-ELECTRICAL DEVICES

This invention relates to opto-electrical devices, for example devices for emitting or detecting light.

One specific class of opto-electrical devices is those that use an organic material for emission or detection of light. Suitable organic materials are described in PCT/WO90/13148 and US 4,539,507, the contents of both of which are incorporated herein by reference. The basic structure of these devices is a light-emissive organic layer sandwiched between two electrodes. In a light-emissive device one of the electrodes (the cathode) injects negative charge carriers (electrons) and the other electrode (the anode) injects positive charge carriers (holes). The electrons and holes combine in the organic layer generating photons. In PCT/WO90/13148 the organic material is a polymer such as poly(p-phenylenevinylene ("PPV"), . In US 4,539,507 the organic material is of the class known as small molecule materials, such as (8-hydroxyquinoline)aluminium ("Alq3").

Figure 1 shows a typical cross-sectional structure of such a device, in this case an organic light-emissive device ("OLED"). The typical OLED is fabricated on a glass or plastic substrate 1 coated with an electrically conductive material to form an anode 2. Such coated substrates are commercially available. The coated substrate is covered with at least a thin film of an electroluminescent organic material 3 and a final cathode layer 4, which is typically a metal or alloy. There may be an additional conductive layer 5 for improving transport of charge from the anode to the active layer 3 of the device. Similar device structures are used for devices intended for the detection of light and its conversion to charge flow.

Some particularly attractive applications of OLEDs are as displays in battery-powered apparatus such as portable computers and mobile phones. In order to extend the battery life of such apparatus there is a drive to increase the efficiency

of the light-emissive devices. One route to improving efficiency is by careful choice and design of the light-emissive material itself. Another is by optimising the physical layout of the display. A third is by improving the conditions for charge injection into and charge recombination in the emissive layer. To improve the conditions for charge injection into and charge recombination in the emissive layer it is known to select the materials of the electrodes to have energy levels and work functions that aid the desired flow of charge carriers.

In most devices at least one of the electrodes is light-transmissive to allow photons either to enter the device for detection or to leave the device after having been generated. Most display devices are opaque, and for those devices only one of the electrodes (the front electrode) needs to be light-transmissive. This is convenient because optimising the materials and physical design of an electrode for both charge injection and transparency is difficult.

For optimal performance the cathode electrode should have a low work function. A commonly used low work function cathode is formed of a layered composite of lithium and aluminium. A low work function layer of lithium is provided on the side of the cathode nearer to the active layer. This is backed by a layer of aluminium which imparts greater conductivity across the area of the cathode. This design has good charge injection performance but suffers from three principal problems. First, since lithium and its normal substitutes such as calcium are highly reactive considerable precautions must be taken in manufacturing of the cathode, and there may be a tendency to unwanted reactions in between the lithium (or substitute) and other layers of the device. Second, a cathode electrode of this type is opaque, which in most applications limits the choice of anode to a light-transmissive structure. Third, a cathode of this type can not be used to manufacture a light-transmissive display — which could be used for applications such as pilots' or drivers' head-up displays, where it could be laminated over a window or screen.

One light-transmissive cathode structure that has been used is a thin layer of calcium backed by a layer of ITO (indium-tin oxide), with the calcium layer closer to the active region of the device. Another technique is to use a similar thin calcium layer as a diffusion barrier for a layer of ZnS (see US 5,739,545). Both of these approaches still require the use of a highly reactive material.

It would be desirable for there to be a cathode that is capable of addressing the above problems.

According to one aspect of the present invention there is provided an opto-electrical device comprising an anode electrode; a light-transmissive cathode electrode; and an opto-electrically active region of organic material located between the electrodes; the cathode electrode including an electrically conductive layer and a spacing layer comprising an electrically non-conductive material, the spacing layer being located between the electrically conductive layer and the opto-electrically active region and being sufficiently thin to allow charge to flow through it between the electrically conductive layer and the active region.

According to a second aspect of the present invention there is provided a method for forming an opto-electrical device, the method comprising: depositing an anode electrode; depositing over the anode electrode a region of an opto-electrically active organic material; depositing over the region of opto-electrically active material an electrically non-conductive material to a thickness in the range from 0.5 to 20 nm to form a first cathode layer; and depositing over the first cathode layer an electrically conductive layer to form a second cathode layer.

The electrically conductive layer suitably has an electrical conductivity greater than 10^5 ($\Omega \cdot \text{cm}$) $^{-1}$. The electrically conductive layer could comprise a metal and/or a conductive oxide and/or a conductive organic (preferably polymer) material. The electrically conductive layer could comprise one or more of the following materials: Al, Au, Cu, Ag, Pt, PEDOT:PSS, ITO, TO (tin oxide), IZO. The electrically conductive layer may comprise one or more electrically conductive sub-layers of

different compositions. The one of such sub-layers closest to the layer of non-conductive material may preferably comprise a metal and/or a conductive organic material. Where the material of that sub-layer is not light-transmissive in the bulk the layer is suitably sufficiently thin to permit the transmission of light through it; suitably the thickness of that layer is in the range from 2 to 20 nm. The one of such layers furthest from the layer of non-conductive material may preferably comprise a conductive material that is light-transmissive in the bulk, such as ITO, TO, NiO or other conductive oxides, poly(aniline) in its conductive state or PEDOT:PSS, or other materials such as ZnSe and ZnS, or a combination of any two or more of those materials together optionally with other materials.

The said electrically non-conductive material may comprise two or more non-conductive components. The spacing layer may consist of or consist essentially of the said electrically non-conductive material (possibly together with any impurities). Alternatively the spacing layer may additionally comprise an electrically conductive material. Suitably such an electrically conductive material is combined intimately and preferably substantially uniformly throughout the spacing layer. The spacing layer is suitably electrically non-conductive across its area but may be electrically conductive, at least to some extent, through its thickness, for example as a result of the possibility of tunnelling through the layer. The thickness of the spacing layer is suitably in the range from 0.5 to 20 nm. Where the spacing layer comprises an electrically conductive material (together with the said non-conductive material) the thickness may preferably be in the range from 2 to 20 nm (most preferably from 4 to 8 nm); otherwise the thickness of the spacing layer is preferably in the range from 0.5 to 10 nm (most preferably from 0.8 to 3 nm).

The electrically non-conductive material may be an oxide or fluoride of a group 1 metal such as lithium or caesium. The layer may consist substantially of that material or may consist of that material together with any impurities. The layer may additionally comprise a metal.

The work function of the cathode at its surface closer to the active region is suitably less than 3.5 eV and preferably less than 3.0 eV.

The anode may be light-transmissive, preferably transparent. The anode may comprise one or more of tin oxide (TO), indium-tin oxide (ITO) or gold. The cathode may be light-transmissive, preferably transparent. Any sub-layer of the cathode may be light-transmissive, preferably transparent. The device may be light-transmissive or opaque.

The opto-electrically active region may be light-emissive or (suitably on the application of a suitable electric field across it) or may be light-sensitive (suitably generating an electric field in response to incident light). The opto-electrically active region suitably comprises a light-emissive material or a light-sensitive material. Such a light-emissive material is suitably an organic material and preferably a polymer material. The light-emissive material is preferably a semiconductive, and/or conjugated polymer material. Alternatively, the light-emissive material could be of other types, for example sublimed small molecule films or inorganic light-emissive material. The or each organic light-emissive material may comprise one or more individual organic materials, suitably polymers, preferably fully or partially conjugated polymers. Example materials include one or more of the following in any combination: poly(p-phenylenevinylene) ("PPV"), poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), one or more PPV-derivatives (e.g. di-alkoxy or di-alkyl derivatives), polyfluorenes and/or co-polymers incorporating polyfluorene segments, PPVs and related co-polymers, poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)) ("TFB"), poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-methylphenyl)imino)-1,4-phenylene-((4-methylphenyl)imino)-1,4-phenylene)) ("PFM"), poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene)) ("PFMO"), poly(2,7-(9,9-di-n-octylfluorene) ("F8") or (2,7-(9,9-di-n-octylfluorene)-3,6-Benzothiadiazole) ("F8BT"). Alternative materials include small molecule materials such as Alq3.

There may be one or more other layers in the device. There may be one or more charge transport layers (preferably of one or more organic materials) between the active region and one or other of the electrodes. The or each charge transport layer may suitably comprise one or more polymers such as polystyrene sulphonic acid-doped polyethylene dioxythiophene ("PEDOT-PSS"), poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) ("BFA"), polyaniline and PPV.

The present invention will now be described by way of example with reference to the accompanying drawing, in which: figure 2 is a cross-section of a light-emissive device. The illustrated thicknesses of the layers in figure 2 are not to scale.

The device of figure 2 comprises an anode electrode 10 and a cathode electrode 11. Located between the electrodes is an active layer 12 of light-emissive material. A charge transport layer 13 of PEDOT:PSS is located between the anode electrode 10 and the light-emissive layer 12. The device is formed on a glass substrate 14.

The cathode electrode comprises at least two layers. The layer 11a nearer to the light-emissive material 12 is a very thin transparent layer of CsF. The layer 11b further from the light-emissive material 12 is a thin semi-transparent layer of Al. Although CsF is non-conductive in the bulk, the layer 11a is sufficiently thin that charge may pass through it between the layer 11b and the light-emissive material 12. This cathode structure of layers 11a and 11b is light-transmissive. This structure has been found to yield a substantial increase in performance over certain prior light-transmissive cathodes, which can be attributed - at least in part - to the relatively low work function exhibited by the cathode. Furthermore, the cathode does not include any highly reactive materials, and especially not adjacent to the relatively sensitive organic emissive layer 12.

To form the device of figure 2 a transparent layer of ITO to form the anode electrode 10 may first be deposited on a sheet of glass 14. The glass sheet could be a sheet of sodalirne or borosilicate glass of a thickness of, for instance, 1mm. The thickness of the ITO coating is suitably around 100 to 150nm and the ITO suitably has a sheet resistance of between 10 and 30 Ω/\square . ITO-coated glass substrates of this type are commercially available. As an alternative to glass, the sheet 14 could be formed of perspex. As an alternative to ITO, gold, TiO, NiO, Pd, Pt etc. could be used as the anode.

Over the ITO anode is deposited a hole transport or injecting layer 13. The hole transport layer is formed from a solution containing PEDOT:PSS with a ratio of PEDOT to PSS of around 1: to 5.5. The thickness of the hole transport layer is suitably around 500 Å. The hole transport layer is spin-coated or blade-coated from solution and then baked at around 200°C for 1 hour in a nitrogen environment. The hole 13 substrate structure is a typical structure for an LED device, the two distinct layers of sequentially deposited materials being clearly visible.

Then the electroluminescent layer 12 is deposited. In this example, the electroluminescent layer is formed of 20% TFB, 80% 5F8BT blended together. The term 5F8BT refers to:

poly (2,7-(9,9-di-n-octylfluorene) ("F8")

doped with 5%

poly-(2,7-(9,9-di-n-octylfluorene)-3,6-benzothiadiazole) ("F8BT").

The term TFB refers to a copolymer of 1,4-phenylene and 4,4'-biphenylene.

poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)).

This mixture is coated over the hole transport layer by spin-coating typically to a thickness of around 750 Å. Other materials such as PPV could be used for the emissive layer. The emissive layer could be formed by other routes such as blade or meniscus coating and could be deposited in precursor form if desired.

The cathode is then deposited. The two distinct layers of the cathode are deposited by successive thermal evaporation steps *in vacuo*. First the CsF layer

11a is deposited directly over the TFB/5F8BT layer 12 to a thickness of around 1 nm. Then, in a second thermal evaporation step the Al layer 11b is deposited directly over the CsF layer 11a to a thickness of 10 to 20 nm. Preferably the vacuum is not broken between the deposition steps. Sputtering is one less preferred alternative to evaporation for the deposition process. The two material layers could be graded to form a compositionally varying mixture or alloy.

One or more encapsulant layers 20 of one or more dielectric materials such as SiO_2 , Si_3N_4 , AlN or SiO_xN_y (silicon oxynitride) are then deposited over the cathode 11 to inhibit oxidation of the cathode, and especially the Al layer 11b. The dielectric layers could be deposited by chemical vapour deposition (CVD) or low pressure CVD or any other suitable process.

Finally, contacts are attached to the anode layer 10 and to the rearmost layer of the cathode and the device is preferably sealed in epoxy resin for further environmental protection.

In use, when a suitable voltage is applied between the anode and the cathode the light-emissive layer is stimulated to emit light. This can pass to a viewer through the light-transmissive anode and the glass cover sheet and/or through the light-transmissive cathode (see arrows 30).

As an alternative to CsF, other dielectric materials such as LiF, Li_2O , or a composite of two or more such materials together, optionally, with one or more metals such as Al or Ag could be used for the layer 11a. The thickness of the layer 11a is preferably great enough for the layer 11a to have an influence on the work function of the cathode, at least on the side of the cathode closer to the active layer of the device. For example, the effective work function of a LiF / Al cathode may be around 2.5 eV. The thickness of the layer 11a is preferably small enough for the layer 11a not to obstruct too greatly flow of charge between the electrically conductive layer 11b and the active layer 12. Typically, thicknesses in the range from 0.5 to 20 nm (depending on the conductivity of the layer 11a) could

be considered preferable for balancing these factors. The layer 11a could be formed from a composite of a metal and a dielectric material, for example Al co-deposited with CsF.

As an alternative to Al, other electrically conductive materials such as Au or Ag could be used for the layer 11b. The thickness of the layer 11b is preferably great enough for the cathode as a whole to be adequately conductive across its area, but not so great that the cathode becomes opaque. Typically, thicknesses in the range from 2 to 20 nm could be considered preferable for balancing these factors. If, for example in a device of larger area, the required conductivity of the cathode could not be achieved (which could lead to non-uniform charge injection across the area of the device) then one or more additional layers 11c of light-transmissive conductive materials could be deposited on the outer surface of the layer 11b. These layers could be formed of one or more inorganic or organic materials such as indium-tin oxide (ITO), tin-oxide (TO), indium-zinc oxide (IZO) or PEDOT:PSS.

Where a layer 11c is present the layer 11b could be omitted. Since the layer 11c may be a composite layer the following non-limiting summary indicates some of the broad classes of structures that may be used for the cathode:

◀ Further from active layer ▶ Closer to active layer ▶

1	Transparent conductor	Thin insulating layer
2	Transparent conductor	Metal layer
3	Transparent conductor	Conductive plastics layer
4	Transparent conductor	Conductive plastics layer
5	Transparent conductor	Metal: thin insulating layer composite
6	Transparent conductor	Conductive plastics layer
		Metal: thin insulating layer composite

These structures all have in common a thin layer comprising an insulating material and, further from the active layer of the device, a conductive layer. The cathode and each layer of it could be non-light-transmissive, especially where the anode of the device is light-transmissive.

Where one or more dielectric layers 20 is present, it may serve to modify the optical cavity of the device to enhance colour (by a mechanism such as line narrowing) or emission angle. The principals of these effects are described, for example, in GB 2,320,105 A, the contents of which are incorporated herein by reference.

The anode structure could be varied. For example, the PEDOT:PSS layer 13 could be omitted, and/or the ITO layer could be replaced by another light-transmissive or opaque material. One example of an alternative anode structure is for the ITO layer to be replaced by a composite laminated structure comprising a

layer of Al further from the active layer 12 and a layer of Pt closer to the active layer 12.

Any suitable light-emissive material or combination thereof could be used for layer 12. The emissive material could be of the class of sublimed molecular films, as described for example in "Organic Electroluminescent Diodes", C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* 51, 913-915 (1987).

A device of the type described above may form a single pixel of a multi-pixel display device. The pixels could be addressed in the known passive or active matrix schemes by patterning of one or both electrodes and/or provision of drive circuitry (e.g. thin-film transistor (TFT) circuitry) on the display plane itself. The TFT or other drive circuitry could be provided by devices such as transistors (e.g. FETs) of silicon or other organic or inorganic semiconductors. Such circuitry may be transparent and could be located at the anode or more normally the cathode of the device, but when not, the structure is top emitting if electronics are built into the substrate.

Applications of the devices described above include display devices. Where both the anode and the cathode electrodes are light-transmissive then the display device may be a translucent display device. This may find application in head-up displays, autocues, and other such devices. For a head-up display, a device of the type described herein (preferably a multi-pixel device) could form or be mounted to the visor of a helmet, a cockpit window or a screen located between a pilot and a window.

The same principals may be applied to devices for the detection rather than the generation of light. By replacing (if necessary) the light-emissive material with a material that is capable of generating an electrical field or current in response to light the improved characteristics of the improved electrodes as described above may be used to enhance detection voltages and/or efficiency.

The applicant draws attention to the fact that the present invention may include any inventive feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof, without limitation to the scope of any of the present claims. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. An opto-electrical device comprising:
 - an anode electrode;
 - a light-transmissive cathode electrode; and
 - an opto-electrically active region of organic material located between the electrodes;the cathode electrode including an electrically conductive layer and a spacing layer comprising an electrically non-conductive material, the spacing layer being located between the electrically conductive layer and the opto-electrically active region and being sufficiently thin to allow charge to flow through it between the electrically conductive layer and the active region.
2. An opto-electrical device as claimed in claim 1, wherein the electrically conductive layer has an electrical conductivity greater than 10^5 ($\Omega \cdot \text{cm}$) $^{-1}$.
3. An opto-electrical device as claimed in claim 1 or 2, wherein the electrically conductive layer has a thickness in the range from 0.5 to 20 nm.
4. An opto-electrical device as claimed in any preceding claim, wherein the electrically conductive layer comprises Ag, Al, Cu or Pt.
5. An opto-electrical device as claimed in any preceding claim, wherein the spacing layer is electrically non-conductive across its area.
6. An opto-electrical device as claimed in any preceding claim, wherein the electrically non-conductive material is an oxide or fluoride of a group I metal.
7. An opto-electrical device as claimed in any preceding claim, wherein the spacing layer comprises a metal.

8. An opto-electrical device as claimed in any preceding claim, wherein the thickness of the spacing layer is in the range from 0.5 to 20 nm.
9. An opto-electrical device as claimed in any preceding claim, comprising a second electrically conductive layer between the said electrically conductive layer and the spacing layer.
10. An opto-electrical device as claimed in claim 9, wherein the second electrically conductive layer comprises a metal.
11. An opto-electrical device as claimed in claim 10, wherein the second electrically conductive layer has a thickness in the range from 2 to 20 nm.
12. An opto-electrical device as claimed in claim 11, wherein the opto-electrically active region is light-emissive.
13. An opto-electrical device as claimed in any preceding claim, wherein the opto-electrically active region comprises a light-emissive organic material.
14. An opto-electrical device as claimed in claim 13, wherein the light-emissive organic material is a polymer material.
15. An opto-electrical device as claimed in claim 14, wherein the light-emissive organic material is a conjugated polymer material.
16. An opto-electrical device as claimed in any of claims 12 to 15, comprising a charge transport layer between the light-emissive organic material and one of the electrodes.
17. A method for forming an opto-electrical device, the method comprising:
depositing an anode electrode;

depositing over the anode electrode a region of an opto-electrically active material:

depositing over the region of opto-electrically active material an electrically non-conductive material to a thickness in the range from 0.5 to 20 nm to form a first cathode layer; and

depositing over the first cathode layer an electrically conductive layer to form a second cathode layer.

18. An opto-electrical device substantially as herein described with reference to figure 2 of the accompanying drawings.

19. A method for forming an opto-electrical device substantially as herein described with reference to figure 2 of the accompanying drawings.



The
Patent
Office
UK



Application No: GB 9907118.5
Claims searched: 1-19

Examiner: Miss E.L.Rendle
Date of search: 21 June 1999

INVESTOR IN PEOPLE

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): H1K (KEAL, KEAX, KEBCA, KEBCS, KEBCX, KEBX)

Int Cl (Ed.6): H01L 51/20; H05B 33/26, 33/28

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	WO 96/29747 A1	(OHIO STATE UNIVERSITY) see whole document, especially page 5 lines 5-18, page 6 lines 3-10, page 6 line 32-page 7 line 2, page 7 lines 11-21, page 13 lines 15-35, page 15 lines 6-12 and page 15 line 24 to page 16 line 4.	1, 2, 3, 4, 5, 8, 12, 13, 14, 15, 16, 17
X	WO 96/26830 A1	(OHIO STATE UNIVERSITY) see whole document, especially page 6 line 6 to page 7 line 6, and page 12 line 17 to page 14 line 10.	1, 2, 3, 4, 5, 8, 12, 13, 14, 15, 16, 17.
A	US 5 714 838	(IBM) see figure 2.	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.